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The behavior of radioactive metals (Am, Eu, Sr) during the processing of radioactive graphite in salt melts

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Abstract. The behavior of Am, Eu, Sr radionuclides was investigated by thermodynamic modeling method at heating of radioactive graphite in NaCl – KCl – Na₂CO₃ – K₂CO₃ molten salt with additives of nickel oxide NiO. The integrated thermodynamic analysis was carried out by means of TERRA software in temperature range 373-3273 K to determine possible composition of condensed and gaseous phases. It was established that americium is in gaseous state in temperature range 2773-3273 K. Europium is in the forms of gaseous EuO and Eu in temperature range 2373-3273 K. Strontium is in the forms of gaseous SrCl₂, SrCl, Sr, SrO in temperature range 2373-3273 K.

1. Introduction

Graphite is widely used in designs of nuclear reactors (uranium-graphite water- and gas-cooled plants) as a moderator of neutrons and structural material of the reactor core. The operation resource of the majority of nuclear power units will be exhausted in the next 10-15 years. Decommissioning of the uranium-graphite reactors represents a complex of tasks connected with the problem of choice of optimum methods of radioactive waste (RW) processing. The treatment of irradiated reactor graphite is one of the critical tasks. Final treatment of reactor graphite (its disposal) is complicated by the existence of long-lived radionuclides in it. Such radionuclides include ¹⁴C (radioactive half-life is 5730 years) which forms 95% of graphite activity. The activity of graphite is also defined by the following radionuclides (²⁴¹Am, ⁹⁰Sr, ¹⁵⁴Eu and others) [1]. There are about 250 thousand tons of accumulated irradiated reactor graphite in the world (figure 1) [2]. The problem of the processing of irradiated reactor graphite is especially relevant for Great Britain — 86 thousand tons, Russia — 60 thousand tons, the USA — 55 thousand tons and France — 23 thousand tons. The majority of uranium-graphite reactors must be isolated and have controlled maintenance for more than 80 years as there are no reasonable approaches to treatment of reactor graphite [2]. At the same time such options as disposal and graphite processing are considered. Investigations of the opportunities of the graphite purification from radionuclides by thermal action of various liquid and gaseous media, alkalis, acids, molten salts, vapor, helium, nitrogen, air, argon are carried out in Russia and abroad (“Carbowaste” project). According to experts, the processing of irradiated graphite will give RW ready for disposal of 1-2% from the initial graphite volume [1].

The purpose of this research work is the determination of equilibrium composition of condensed and gaseous phases in the interaction of radioactive graphite with metal oxide and molten salts in the



wide temperature range. The task of the study is carrying out thermodynamic model operation of the considered system.

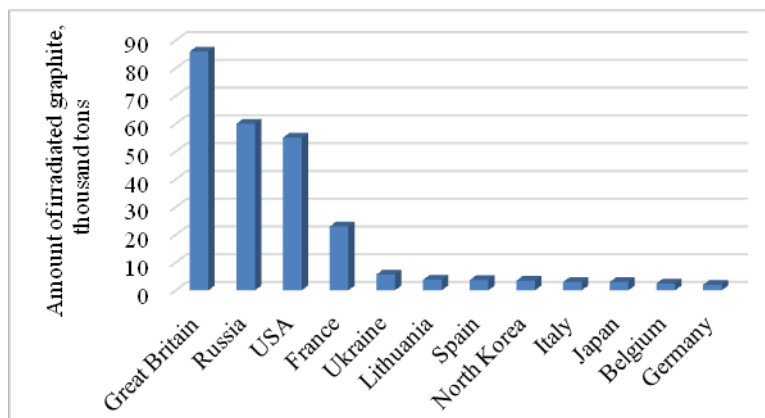


Figure 1. The total amount of accumulated reactor graphite in the world.

2. Calculation procedure

Problems of the investigation of high-temperature processes (for example combustion processes) play a special role for the solution of many technical and scientific problems. A research of these processes by carrying out natural experiments does not always allow to get exact data due to their complexity and errors of measurements. Application of a calculation experiment with use of the personal computer gains the special importance. By means of computer calculations it is possible to analyze various states of a system and to draw conclusions about behavior of the studied objects on the basis of model representations. At the same time the main assumption is that there is a local equilibrium in the system which allows to make calculations with use of a mathematical apparatus of equilibrium thermodynamics.

Thermodynamic model method is an effective and unique method at a research of various high-temperature processes of thermal decomposition, reduction, synthesis. This method was successfully used in works [3-9].

The research of behavior of radioactive metals (Am, Eu, Sr) which are contained in reactor graphite was carried out by thermodynamic model method by means of TERRA software [10,11]. The program allows to investigate the arbitrary in chemical composition systems on the basis of reference information about thermochemical and thermodynamic properties of the individual substances systematized at Institute of High Temperatures of RAS (INVATERMO database), national US Bureau of Standards, calculated in Moscow State Technical University according to molecular calorimetric and spectrochemical data [12,13].

Thermodynamic model operation was carried out at initial pressure of 0.1 MPa, at initial temperature 373 K and final temperature 3273 K. Temperature measurement interval was 100 K. The composition of the initial system for thermodynamic calculations was the following: gaseous phase (argon), condensed phase (metal oxide (NiO) and molten salt ($\text{NaCl} - \text{KCl} - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$), radioactive graphite ($\text{C} - \text{Am} - \text{Eu} - \text{Sr}$)). The information about initial composition of reactor graphite is taken from works [14,15]. The estimated forms of radionuclides in the studied system are given in Table 1.

Table 1. Assumed radionuclide species

Radionuclide in graphite	Species in equilibrium system
^{12}C , ^{13}C , ^{14}C	$\text{C}_{(\text{cr})}$, $\text{C}_{(\text{g})}$, $\text{CO}_{(\text{g})}$, $\text{CO}_{2(\text{g})}$, $\text{C}_2\text{O}_{(\text{g})}$, $\text{Ni}_3\text{C}_{(\text{cr})}$, $\text{NiCO}_{3(\text{cr})}$, $\text{CCl}_{(\text{g})}$, $\text{ClCO}_{(\text{g})}$, $\text{Cl}_2\text{CO}_{(\text{g})}$, $\text{SrCO}_{3(\text{cr})}$, $\text{Na}_2\text{CO}_{3(\text{cr})}$, $\text{K}_2\text{CO}_{3(\text{cr})}$, $\text{K}_2\text{CO}_{3(\text{g})}$, C^-
^{241}Am , $^{242\text{m}}\text{Am}$, ^{243}Am	$\text{Am}_{(\text{g})}$, $\text{Am}_{(\text{cr})}$, $\text{AmO}_{2(\text{cr})}$, $\text{Am}_2\text{O}_{3(\text{cr})}$, $\text{AmCl}_{3(\text{cr})}$, $\text{AmCl}_{3(\text{g})}$
^{150}Eu , ^{151}Eu , ^{152}Eu , ^{153}Eu , ^{154}Eu , ^{155}Eu	$\text{Eu}_{(\text{cr})}$, $\text{Eu}_{(\text{g})}$, $\text{EuO}_{(\text{cr})}$, $\text{EuO}_{(\text{g})}$, $\text{Eu}_2\text{O}_{3(\text{cr})}$, $\text{EuCl}_{2(\text{cr})}$, $\text{EuOCl}_{(\text{cr})}$, Eu^+ $\text{Sr}_{(\text{cr})}$, $\text{Sr}_{(\text{g})}$, $\text{SrO}_{(\text{cr})}$, $\text{SrO}_{(\text{g})}$, $\text{SrCl}_{(\text{g})}$, $\text{SrCl}_{2(\text{cr})}$, $\text{SrCl}_{2(\text{g})}$, $\text{SrCO}_{3(\text{cr})}$, Sr^+ , SrO^+ , SrCl^+
^{84}Sr , ^{86}Sr , ^{87}Sr , ^{88}Sr , ^{90}Sr ,	Sr^+ , SrO^+ , SrCl^+

3. Results and discussion

Distribution of carbon on phases is presented in figure 2. In temperature range 373-573 K the content of condensed C decreases to ~47 mole%, the content of condensed Na_2CO_3 decreases to ~22 mole% and the content of gaseous CO_2 increases to ~30 mole%, the content of condensed K_2CO_3 increases to ~1 mole%. In temperature range from 573 to 1173 K the content of condensed C decreases to ~12 mole%, condensed Na_2CO_3 — to ~18 mole%, gaseous CO_2 — to zero and the content of gaseous CO increases to ~66 mole%, condensed K_2CO_3 — to ~4 mole%. In temperature range 1173-1273 K the content of condensed C decreases to zero, the content of condensed Na_2CO_3 and condensed K_2CO_3 decreases to ~13 mole% and ~2 mole%, respectively. The content of gaseous CO increases to ~84 mole%, the content of gaseous CO_2 increase to ~1 mole%. In temperature range from 1273 to 1573 K the content of CO decreases to ~69 mole%, the content of condensed Na_2CO_3 and K_2CO_3 decreases to zero, the content of gaseous CO_2 increases to ~31 mole%. In temperature range from 1573 to 2373 K carbon exists in the form of gaseous CO (69 mole%), CO_2 (31 mole%) in the system. In temperature range from 2373 to 3273 K the content of gaseous CO increases to ~92 mole% and the content of gaseous CO_2 decreases to ~8 mole%.

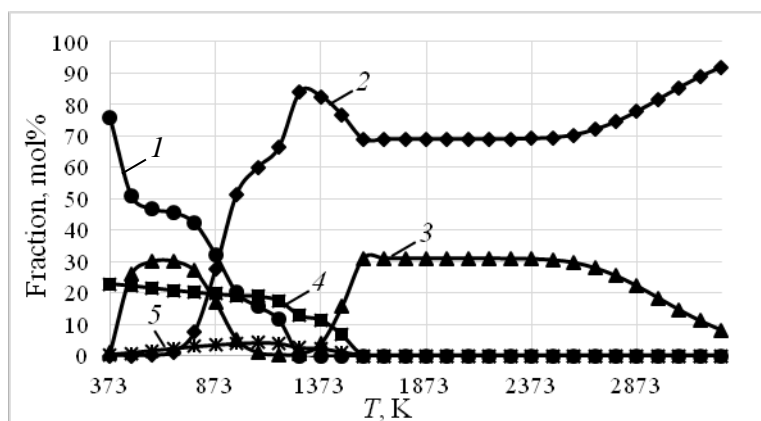


Figure 2. Phase distribution of C: 1 — $\text{C}_{(\text{cr})}$; 2 — $\text{CO}_{(\text{g})}$; 3 — $\text{CO}_{2(\text{g})}$; 4 — $\text{Na}_2\text{CO}_{3(\text{cr})}$; 5 — $\text{K}_2\text{CO}_{3(\text{cr})}$.

Distribution of americium on phases is presented in figure 3. Americium is in the form of condensed AmO_2 up to temperature of 1473 K. In temperature range from 1473 to 2373 K the content of condensed AmO_2 decreases to ~2 mole% and the content of condensed Am_2O_3 increases to ~98 mole%. In temperature range 2373-2473 K the content of condensed AmO_2 decreases to zero, the content of condensed Am_2O_3 decreases to ~93 mole% and the content of gaseous Am increases to ~7 mole%. In temperature range from 2473 to 2673 K the content of condensed Am_2O_3 decreases to zero

and the content of gaseous Am increases to ~100 mole%. The composition of this phase doesn't change up to temperature 3273 K.

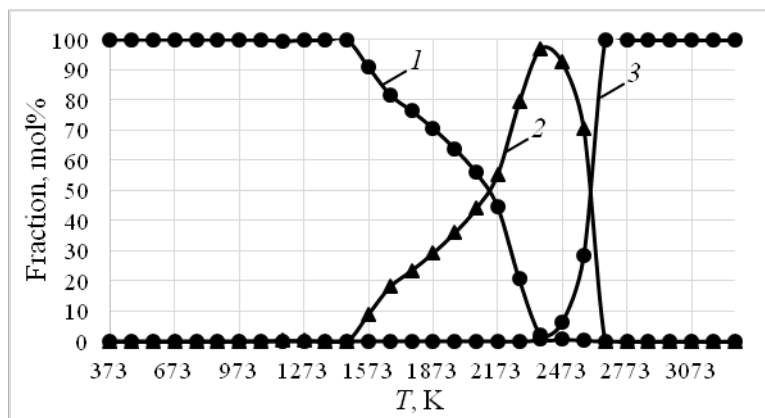


Figure 3. Phase distribution of Am: 1 — $\text{AmO}_{2(\text{cr})}$; 2 — $\text{Am}_2\text{O}_{3(\text{cr})}$; 3 — $\text{Am}_{(\text{g})}$.

Distribution of europium on phases is presented in figure 4. In temperature range from 373 to 773 K the content of condensed EuOCl decreases to ~31 mole% and the content of condensed Eu_2O_3 increases to ~69 mole%. At temperature range from 773 to 873 K the content of condensed EuOCl decreases to ~18 mole% and the content of condensed Eu_2O_3 and EuO increases to ~80 mole% and ~2 mole%, respectively. In temperature range from 873 to 1173 K the content of condensed EuOCl decreases to zero, condensed Eu_2O_3 to ~2 mole% and the content of condensed EuO increases to ~98 mole%. In temperature range from 1173 to 1273 K the content of condensed Eu_2O_3 decreases to ~1 mole% and the content of condensed EuO increases to ~99 mole%. In temperature range from 1273 to 1573 K the content of condensed EuO decreases to ~12 mole% and the content of condensed Eu_2O_3 increases to ~88 mole%. In temperature range from 1573 to 1873 K the content of condensed Eu_2O_3 decreases to ~79 mole% and the content of condensed EuO increases to ~21 mole%. In temperature range 1873 – 1973 K the content of condensed Eu_2O_3 decreases to ~73 mole% and the content of condensed EuO increases to ~26 mole%, the content of gaseous EuO increases to ~1 mole%. In temperature range from 1973 to 2073 K the content of condensed Eu_2O_3 decreases to ~64 mole% and the content of condensed EuO , gaseous EuO , gaseous Eu increases to ~29 mole%, ~6 mole%, ~1 mole%, respectively. In temperature range from 2073 to 2373 K the content of condensed Eu_2O_3 , Eu_2O decreases to zero and the content of gaseous EuO increases to ~90 mole%, the content of gaseous Eu increases to ~10 mole%. In temperature range from 2373 to 2673 K the content of gaseous Eu decreases to ~8 mole% and content of gaseous EuO increases to ~92 mole%. In temperature range 2673-3273 K the content of gaseous EuO decreases to ~80 mole% and the content of gaseous Eu increases to ~20 mole%.

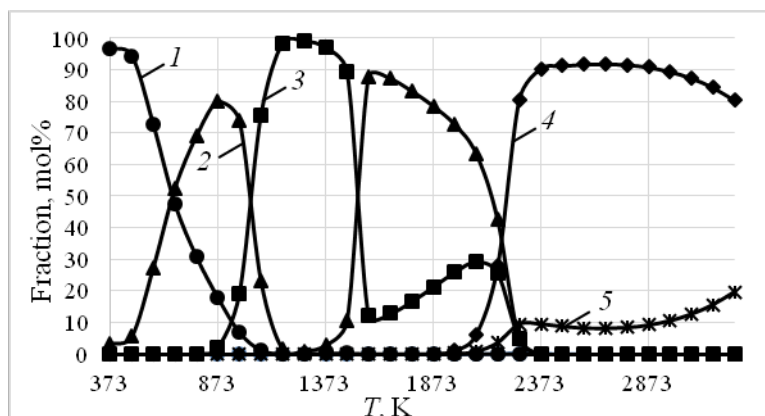


Figure 4. Phase distribution of Eu: 1 — $\text{EuOCl}_{(\text{cr})}$; 2 — $\text{Eu}_2\text{O}_{3(\text{cr})}$; 3 — $\text{EuO}_{(\text{cr})}$; 4 — $\text{EuO}_{(\text{g})}$; 5 — $\text{Eu}_{(\text{g})}$.

Distribution of strontium on phases is presented in figure 5. Strontium is in the form of condensed SrCO_3 up to temperature of 973 K. In temperature range from 973 to 1273 K the content of condensed SrCO_3 decreases to ~2 mole% and the content of condensed SrO increases to ~98 mole%. In temperature range from 1273 to 1473 K the content of condensed SrO decreases to ~97 mole% and the content of condensed SrCO_3 increases to ~3 mole%. In temperature range from 1473 to 1673 K the content of condensed SrCO_3 decreases to ~1 mole% and the content of condensed SrO increases ~99 mole%. In temperature range 1673 — 1773 K the content of condensed SrCO_3 decreases to zero, the content of condensed SrO decreases to ~96 mole% and the content of gaseous SrCl_2 increases to ~4 mole%. In temperature range from 1773 to 1973 K the content of condensed SrO decreases ~60 mole% and the content of gaseous SrCl_2 increases to ~35 mole%, gaseous SrCl — to ~3 mole%, gaseous Sr — to ~2 mole%. In temperature range from 1973 to 2273 K the content of condensed SrO decreases to ~1 mole% and the content of gaseous SrCl_2 increases to ~81 mole%, gaseous SrCl — to ~11 mole%, gaseous Sr — to ~5 mole%, gaseous SrO — to ~2 mole%. In temperature range from 2273 to 2373 K the content of condensed SrO decreases to zero, the content of gaseous SrCl_2 decreases to ~79 mole% and the content of gaseous SrCl increases to ~12 mole%, the content of gaseous Sr increases to ~6 mole%, the content of gaseous SrO increases to ~3 mole%. In temperature range from 2373 to 3273 K the content of gaseous SrCl_2 decreases to ~45 mole% and the content of gaseous SrCl increases to ~26 mole%, gaseous Sr — to ~19 mole%, gaseous SrO — to ~10 mole%.

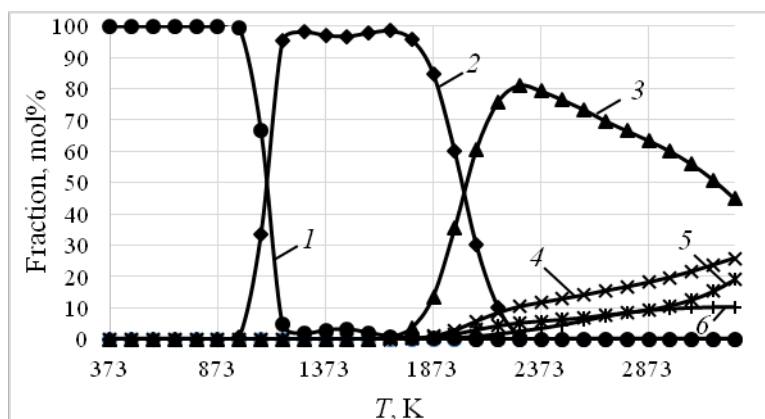


Figure 5. Phase distribution of Sr: 1 — $\text{SrCO}_{3(\text{cr})}$; 2 — $\text{SrO}_{(\text{cr})}$; 3 — $\text{SrCl}_{2(\text{g})}$; 4 — $\text{SrCl}_{(\text{g})}$; 5 — $\text{Sr}_{(\text{g})}$; 6 — $\text{SrO}_{(\text{g})}$.

Oxidation of graphite results in the formation of carbon monoxide and carbon dioxide up to temperature ~1273 K. At temperature >1273 K there is no condensed graphite in the system. The salt

oxide condensed phase enriched with radionuclides disappears at temperature ~2673 K. It is defined that americium contained in radioactive graphite in the form of impurity begins to change into a gaseous phase at temperature ~2673 K, and strontium and europium at temperature ~2373 K.

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